Supporting Information

Zwitterionic d^0 Metal Complexes $[(Cy_2N)_3M]^+[(\mu\text{-}Me)B(C_6F_5)_3]^-$ (M: Ti, Zr, Hf) derived from Tris(dicyclohexylamido)methyl Metal Precursors

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Content

1. X-ray Structure Determination

Table S1 - Crystal structure data for **1-Hf**, **2-Hf**

	1-Hf	**2-Hf**
Empirical formula	$C_{36}H_{66}ClHfN_3$	$C_{37}H_{69}HfN_3$
Formula mass	754.85	734.44
Diffractometer	Bruker Apex II	Bruker Apex II
Crystal dimensions [mm]	0.160 x 0.060 x 0.040	0.245 x 0.100 x 0.080
Colour, habit	colourless, stick	colourless, stick
Crystal system	triclinic	monoclinic
a [Å]	9.7839(3)	9.8267(4)
b [Å]	10.4952(3)	18.5968(8)
c [Å]	39.8958(11)	39.7906(17)
α [°]	86.2460(14)	90
β [°]	83.4103(13)	90.6034(19)
γ [°]	62.6492(13)	90
V [Å]^3	3614.28(19)	7271.1(5)
Space group	*P*-1	*Cc*
Z	4	8
D_{calcd} [Mg·m^{-3}]	1.387	1.342
μ [mm^{-1}]	2.987	2.897
F(000)	1568	3072
λ (Mo-K_α, graphite) [Å]	0.71073	0.71073
Temperature [K]	100(2)	100(2)
θ range for data collection [°]	1.542 to 30.034	2.047 to 30.034
Number of reflections collected	127478	135586
Number of observed reflections [I > 2σ(I)]	17910	20429
Number of independent reflections	21147	21246
Absorptions correction method	numerical	numerical
Max. and min. transmission	0.8995 and 0.6159	0.8229 and 0.5679
Number of data/restraints/parameters	21147 / 0 / 784	21246 / 2 / 732
R indices (all data)	*R*1 = 0.0384	*R*1 = 0.0347
	*wR*2 = 0.0737	*wR*2 = 0.0725
Final *R* indices [I > 2□ (I)]	*R*1 = 0.0503	*R*1 = 0.0371
	*wR*2 = 0.0769	*wR*2 = 0.0731
GoF on F^2	1.137	1.261
Largest difference peak and hole [e·Å^{-3}]	2.833 and -3.685	2.440 and -3.929

Table S2 - Crystal structure data for **3-Ti**, **3-Zr**, **3-Hf**.

	3-Ti	**3-Zr**	**3-Hf**
Empirical formula	$C_{55}H_{69}BF_{15}N_3Ti$ x 2.5 C_7H_8	$C_{55}H_{69}BF_{15}N_3Zr$	$C_{55}H_{69}BF_{15}N_3Hf$ x 1.5 C_6H_{14}
Formula mass	1346.17	1159.16	1375.68
Diffractometer	Bruker Apex II	Bruker Apex II	Bruker Apex II
Crystal dimensions [mm]	0.150 x 0.150 x 0.150	0.240 x 0.120 x 0.080	0.160 x 0.160 x 0.140
Colour, habit	yellow, rhombus	colourless, block	colourless, block
Crystal system	trigonal	orthorhombic	trigonal
a [Å]	16.9270(4)	25.1423(8)	19.1878(6)
b [Å]	16.9270(4)	12.1416(4)	19.1878(6)
c [Å]	39.8167(12)	17.4552(6)	29.1550(12)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	120	90	120
V [Å]^3	9879.9(5)	5328.5(39)	9296.0(7)
Space group	*R*-3	*P*na2$_1$	*R*-3
Z	6	4	6
D_{calcd} [Mg·m^{-3}]	1.358	1.445	1.474
μ [mm^{-1}]	0.218	0.299	1.770
F(000)	4242	2400	4242
λ (Mo-K$_\alpha$, graphite) [Å]	0.71073	0.71073	0.71073
Temperature [K]	100(2)	100(2)	100(2)
θ range for data collection [°]	1.480 to 30.026	1.620 to 25.679	1.410 to 33.722
Number of reflections collected	69469	60344	140003
Number of observed reflections [I > 2σ(I)]	4840	8241	6567
Number of independent reflections	6420	10057	8241
Absorptions correction method	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9655	1.0000 and 0.8770	1.0000 and 0.8835
Number of data/restraints/parameters	6420 / 90 / 352	10057 / 1 / 688	16037 / 0 / 703
R indices (all data)	*R*1 = 0.0482	*R*1 = 0.0371	*R*1 = 0.0356
	*wR*2 = 0.1118	*wR*2 = 0.0679	*wR*2 = 0.0768
Final *R* indices [I > 2□ (I)]	*R*1 = 0.0722	*R*1 = 0.0567	*R*1 = 0.0514
	*wR*2 = 0.1272	*wR*2 = 0.0742	*wR*2 = 0.0825
GoF on F^2	1.002	1.031	1.151
Largest difference peak and hole [e·Å^{-3}]	0.605 and -0.640	0.541 and -0.433	1.834 and -1.239

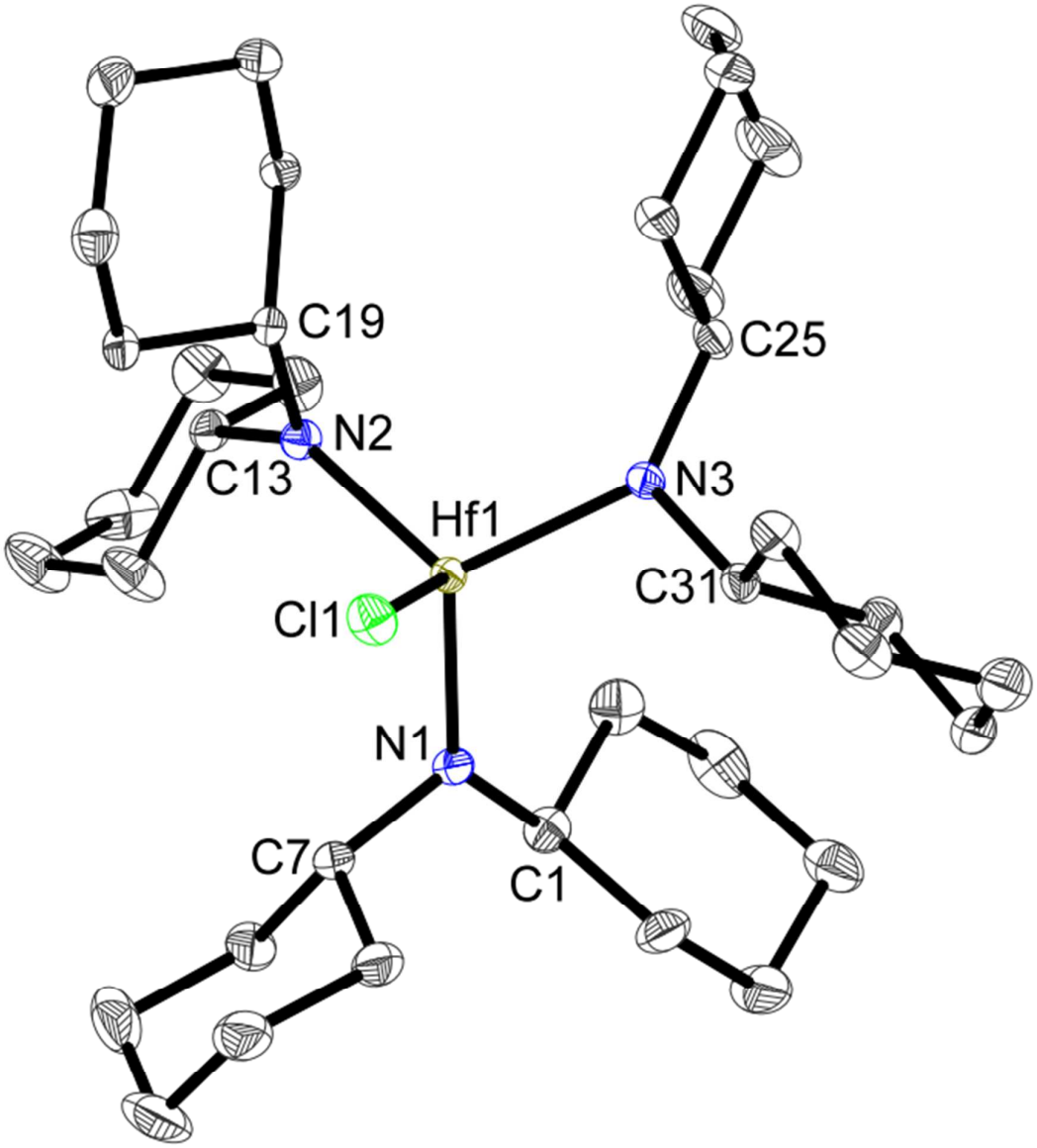

Figure S1 - Molecular structure of complex $ClHf(NCy_2)_3$ (**1-Hf**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the second molecule of the asymmetric unit are omitted for clarity. Selected bond lengths [Å] and angles [°]:Hf1–N1 2.042(3), Hf1–N2 2.022(3), Hf1–N3 2.023(3), Hf1–Cl1 2.4016(8), N1–C1 1.473(4), N1–C7 1.496(4), N2–C13 1.477(4), N2–C19 1.488(4), N3–C25 1.476(4), N1–C31 1.484(4), N1–Hf1–N2 110.32(11), N1–Hf1–N3 113.08(11), N1–Hf1–Cl1 109.34(8), N2–Hf1–N3 111.42(11), Hf1–N1–C1 135.1(2), Hf1–N1–C7 108.0(2), C7–N1–C1 116.8(3), Hf1–N2–C13 138.4(3), Hf1–N2–C19 107.25(19), C13–N2–C19 114.0(3), Hf1–N3–C25 138.4(2), Hf1–N3–C31 106.72(19), C25–N3–C31 114.0(4).

Table S3 - Close intramolecular contacts in complex $ClHf(NCy_2)_3$ (**1-Hf**)

Compound	Close contact	distance [Å]	distance - Σ_{vdW} [Å]
$ClHf(NCy_2)_3$ (**1-Hf**)	Hf1···C7	2.881	-0.819
	Hf1···C19	2.844	-0.856
	Hf1···C31	2.833	-0.867

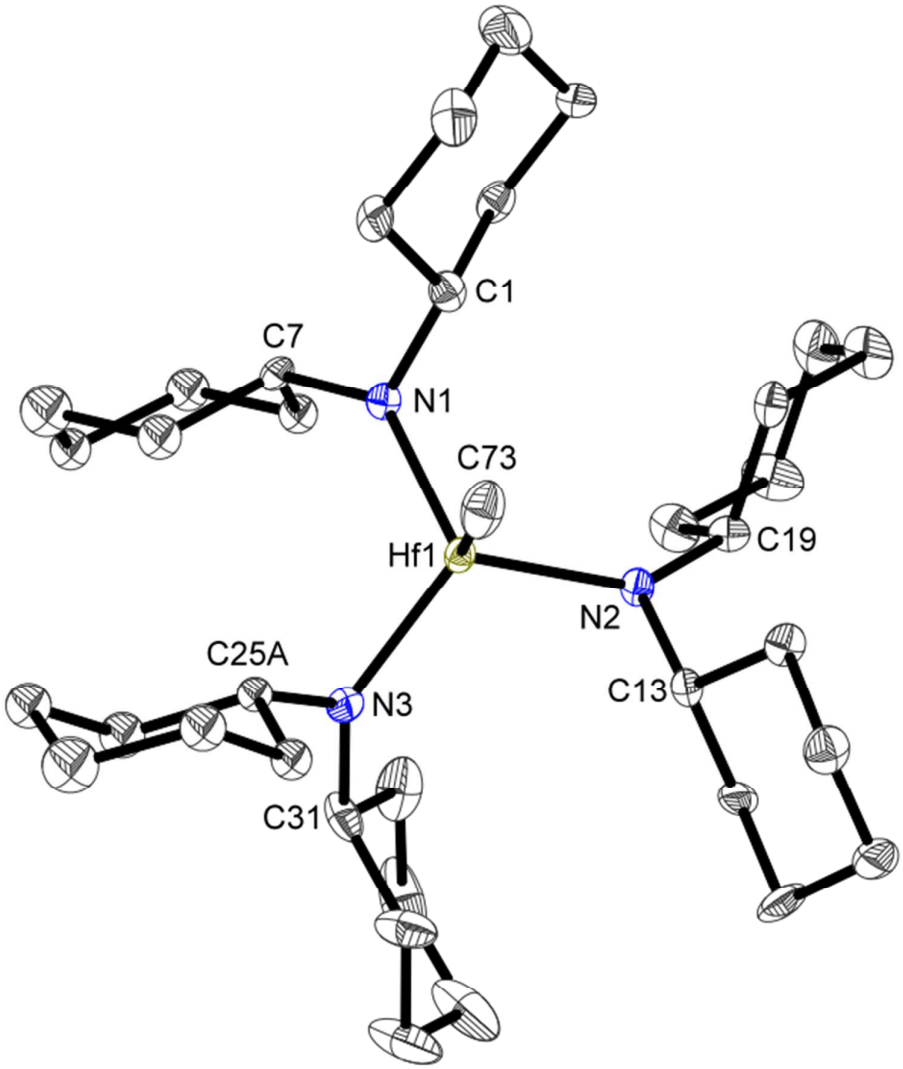

Figure S2 - Molecular structure of complex $MeHf(NCy_2)_3$ (**2-Hf**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, the second position of the disordered part of the molecule and the second molecule of the asymmetric unit are omitted for clarity. Selected bond lengths [Å] and angles [°]: Hf1–N1 2.039(6),Hf1–N2 2.044(6), Hf1–N3 2.051(6), Hf1–C73 2.248(8), N1–C1 1.484(9), N1–C7 1.467(8), N2–C13 1.483(9), N2–C19 1.477(9), N3–C25A 1.548(15), N3–C31 1.466(10), N1–Hf1–N2 112.9(2), N1–Hf1–N3 111.8 (2), N1–Hf1–C73 106.0(3), N2–Hf1–N3 114.2(2), Hf1–N1–C1 107.5(4), Hf1–N1–C7 136.8(4), C7–N1–C1 115.2(5), Hf1–N2–C13 106.6(4), Hf1–N2–C19 139.0(5), C13–N2–C19 114.1(5), Hf1–N3–C25A 105.6(6), Hf1–N3–C31 134.5(5), C25A–N3–C31 119.2(7).

Table S4 - Close intramolecular contacts in complex $MeHf(NCy_2)_3$ (**2-Hf**)

Compound	Close contact	distance [Å]	distance - Σ_{vdW} [Å]
$MeHf(NCy_2)_3$ (**2-Hf**)	Hf1···C1	2.861	-0.839
	Hf1···C13	2.849	-0.851
	Hf1···C25A	2.883	-0.817

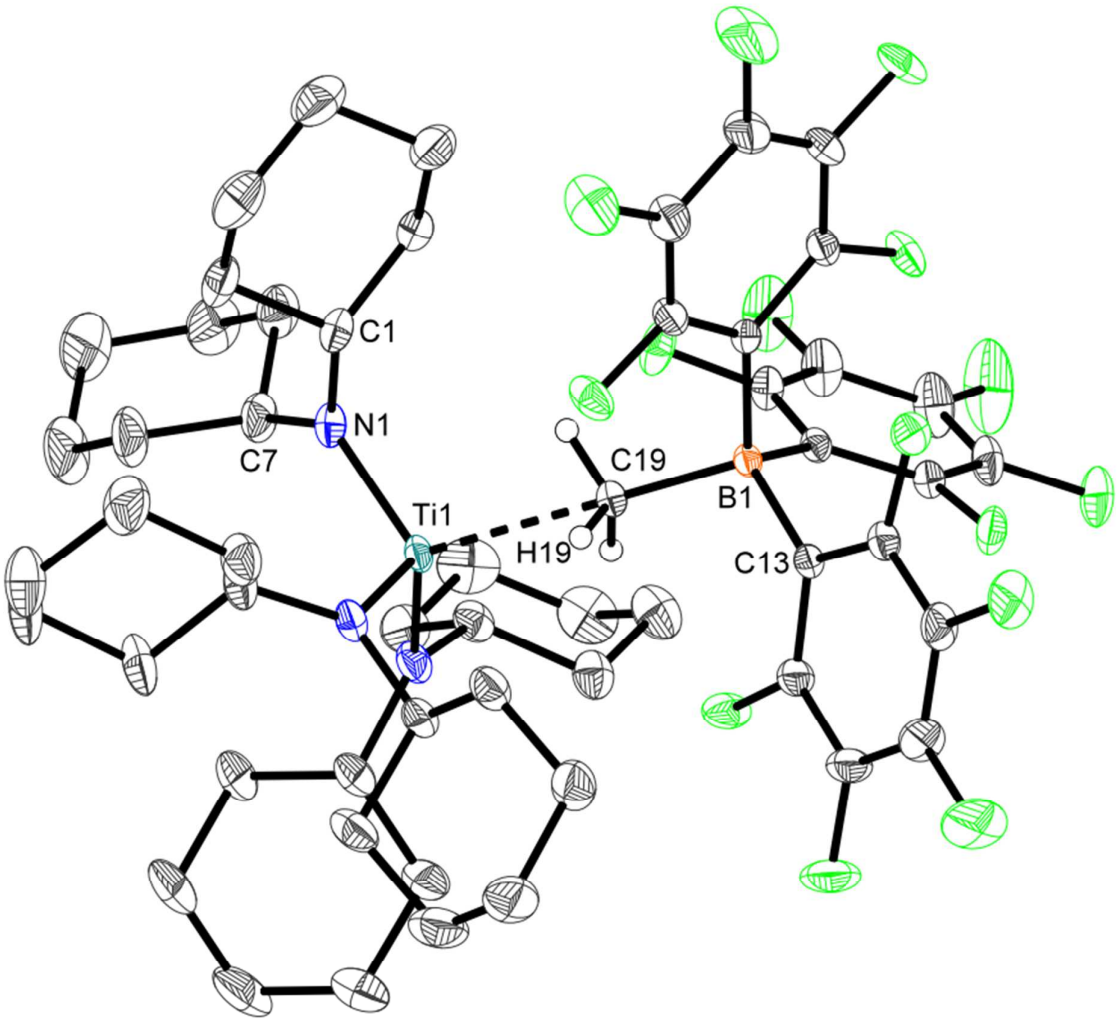

Figure S3 - Molecular structure of complex $[(Cy_2N)_3Ti]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Ti**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (except for H19) and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–N1 1.8850(14), Ti1···C19 2.3786(25), Ti1···H19 2.260(19), N1–C1 1.482(2), N1–C7 1.478(2), B1–C19 1.677(4), C19–H19 0.972(19), B1–C13 1.6496(16), Ti1···C19–B1 180, N1–Ti1···C19 110.339(37), C19–B1–C13 108.52(10), B1–C19–H19 108.8(12), Ti1–N1–C1 112.63(10), Ti–N1–C7 125.01(11).

Table S5 - Close intramolecular contacts in complex $[(Cy_2N)_3Ti]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Ti**)

Compound	Close contact	distance [Å]	distance - Σ_{vdW} [Å]
$[(Cy_2N)_3Ti]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Ti**)	Ti1···C1	2.811	-0.889
	Ti1···C19	2.379	-1.321
	Ti1···H19	2.261	-0.939

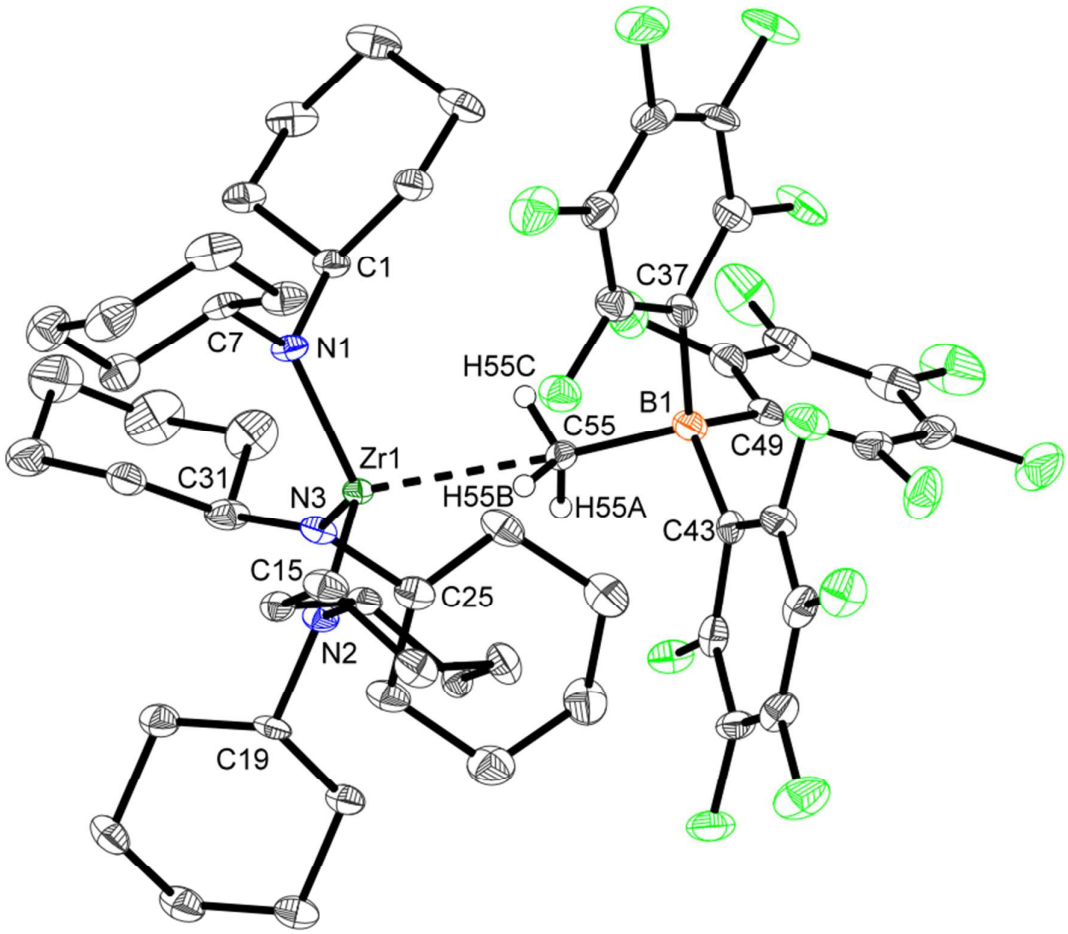

Figure S4 - Molecular structure of complex $[(Cy_2N)_3Zr]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Zr**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (except for H55) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr1–N1 2.038(3), Zr1–N2 2.024(4), Zr1–N3 2.025(3), Zr1···C55 2.569(5), Zr1···H55A 2.53(5), Zr1···H55B 2.36(4), Zr1···H55C 2.36(5), C55–H55A 0.97(5), C55–H55B 0.98(5), C55–H55 C 0.88(5), B1–C55 1.681(7), B1–C37 1.657(6), B1–C43 1.650(7), B1–C49 1.639(7), Zr1···C55–B1 172.6(3), C55···Zr1–N1 102.09(15), C55···Zr1–N2 104.97(16), C55···Zr1–N3 114.84(15), C55–B1–C37 105.6(4), C55–B1–C43 105.9(4), C55–B1–C49 109.8(4), B1–C55–H55A 111(3), B1–C55–H55B 108(3), B1–C55–H55C 111(3).

Table S6 - Close intramolecular contacts in complex $[(Cy_2N)_3Zr]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Zr**)

Compound	Close contact	distance [Å]	distance - Σ_{vdW} [Å]
$[(Cy_2N)_3Zr]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Zr**)	Zr1···C1	2.837	-0.863
	Zr1···C13	2.915	-0.785
	Zr1···C25	2.787	-0.913
	Zr1···C55	2.569	-1.131
	Zr1···H55A	2.525	-0.675
	Zr1···H55B	2.362	-0.838
	Zr1···H55AC	2.367	-0.833

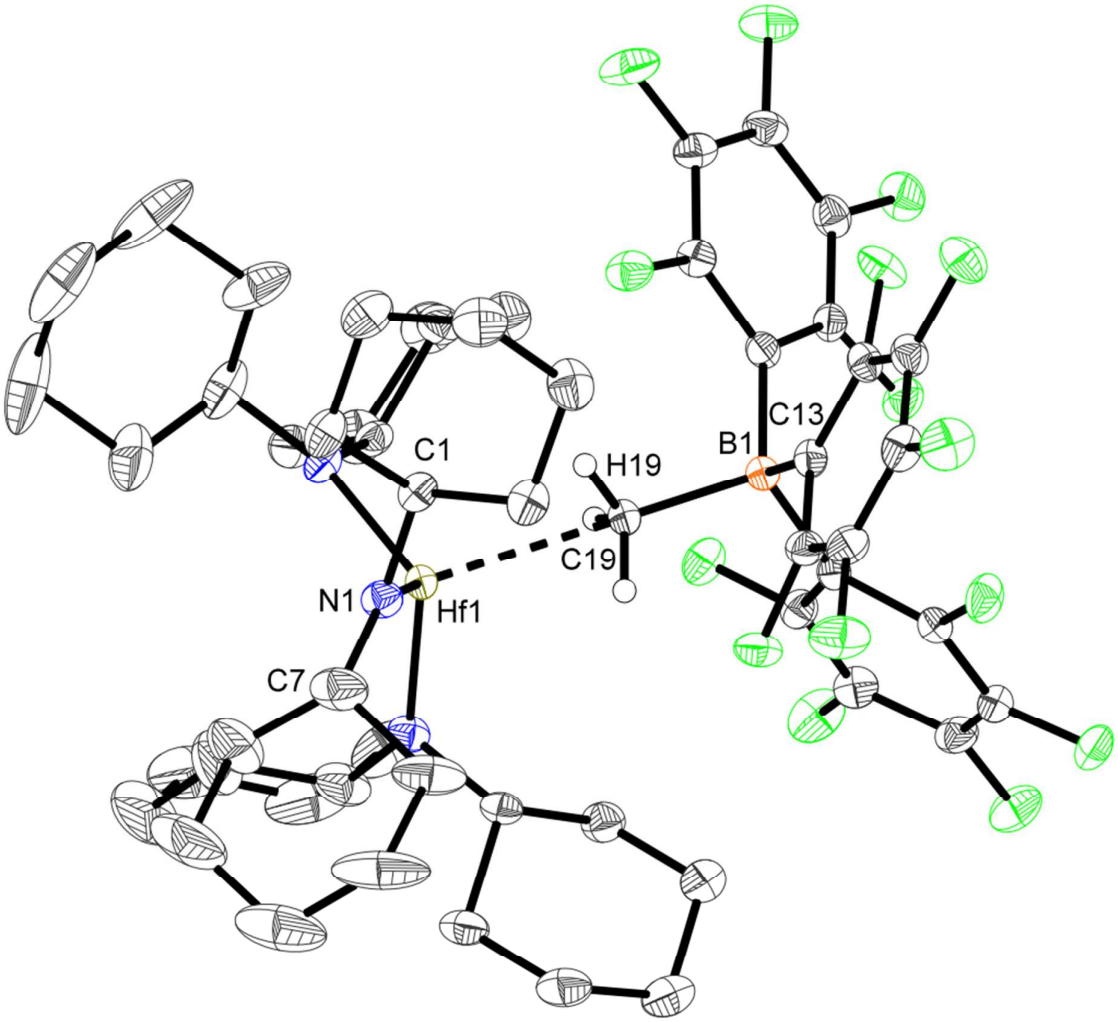

Figure S5 - Molecular structure of complex $[(Cy_2N)_3Hf]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Hf**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (except for H19) and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Hf1–N1 2.0114(18), Hf1···C19 2.502(3), Hf1···H19 2.393(32), N1–C1 1.485(3), N1–C7 1.479(3), B1–C19 1.702(5), C19–H19 0.94(3), B1–C13 1.648(2), Hf1···C19–B1 180, N1–Hf1···C19 107.86(5), C19–B1–C13 107.33(14), B1–C19–H19 107.5(18), Hf1–N1–C1 107.86(5), Hf–N1–C7 138.37(17).

Table S7 - Close intramolecular contacts in complex $[(Cy_2N)_3Hf]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Hf**)

Compound	Close contact	distance [Å]	distance - Σ_{vdW} [Å]
$[(Cy_2N)_3Hf]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Hf**)	Hf1···C1	2.832	-0.868
	Hf1···C19	2.502	-1.198
	Hf1···H19	2.393	-0.807

2. NMR Spectra

2.1 ^{1}H and ^{13}C NMR Spectra of $ClHf(NCy_2)_3$ (**1-Hf**)

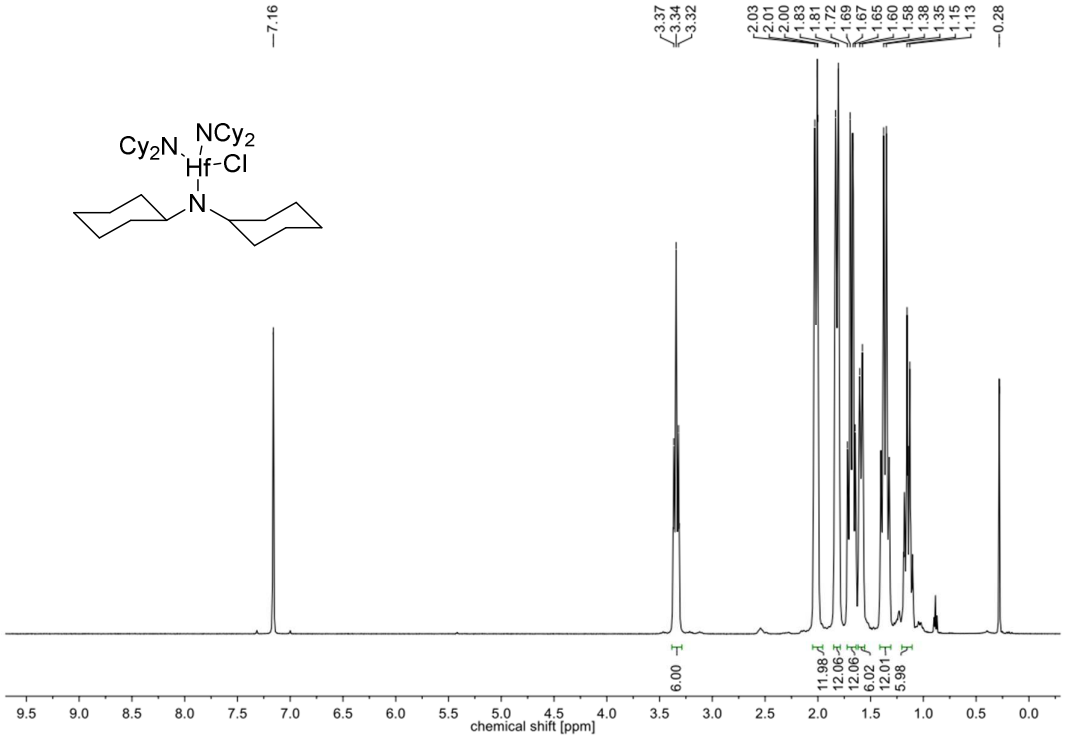

Figure S6 - ^{1}H NMR spectrum of **1-Hf** (499.9 MHz 305.2 K, C_6D_6).

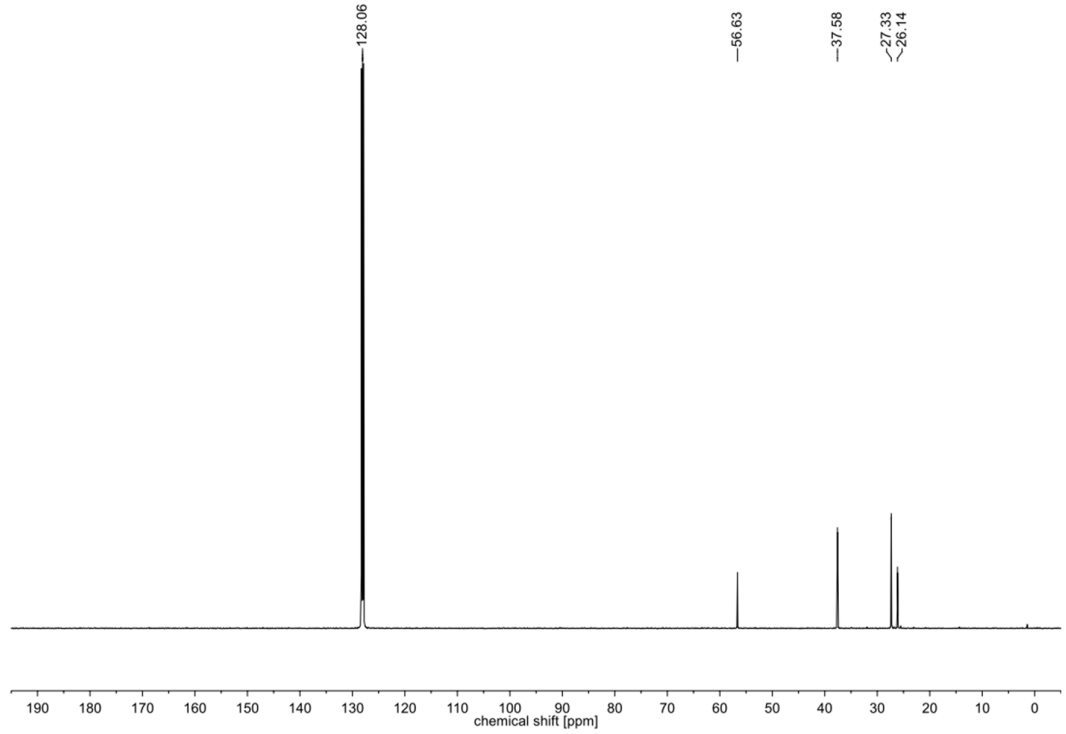

Figure S7 - ^{13}C NMR spectrum of **1-Hf** (125.7 MHz, 305.0 K, C_6D_6).

2.2 ^{1}H and ^{13}C NMR Spectra of $MeHf(NCy_2)_3$ (**2-Hf**)

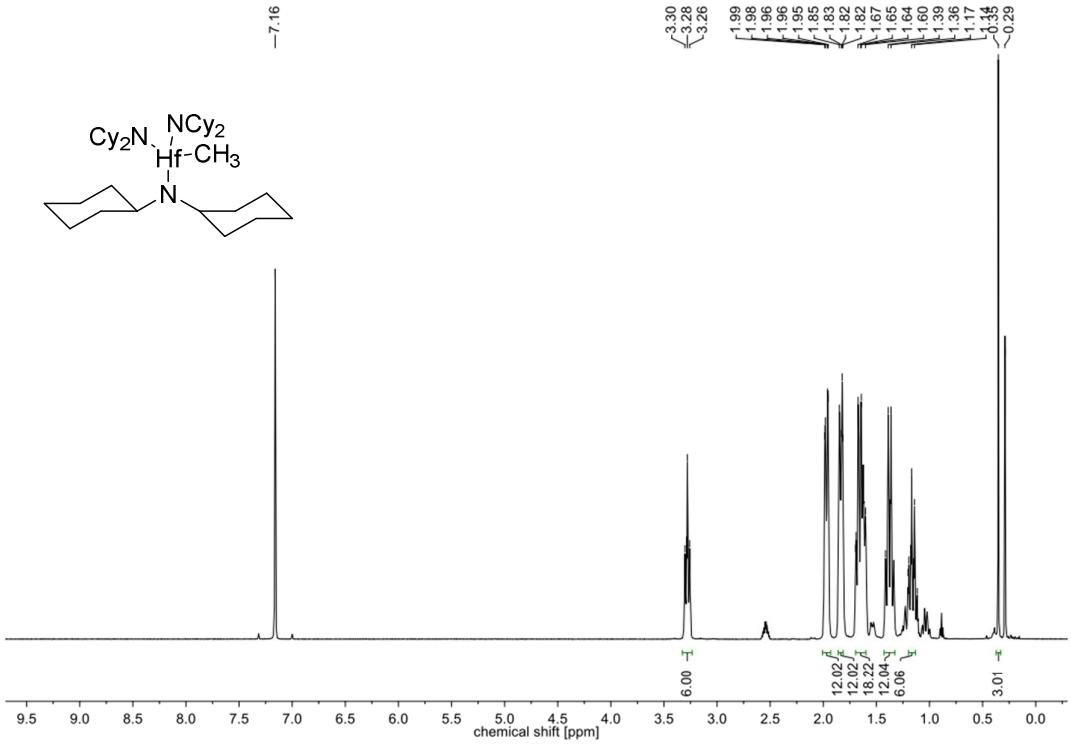

Figure S8 - ^{1}H NMR spectrum of **2-Hf** (499.9 MHz 305.1 K, C_6D_6)

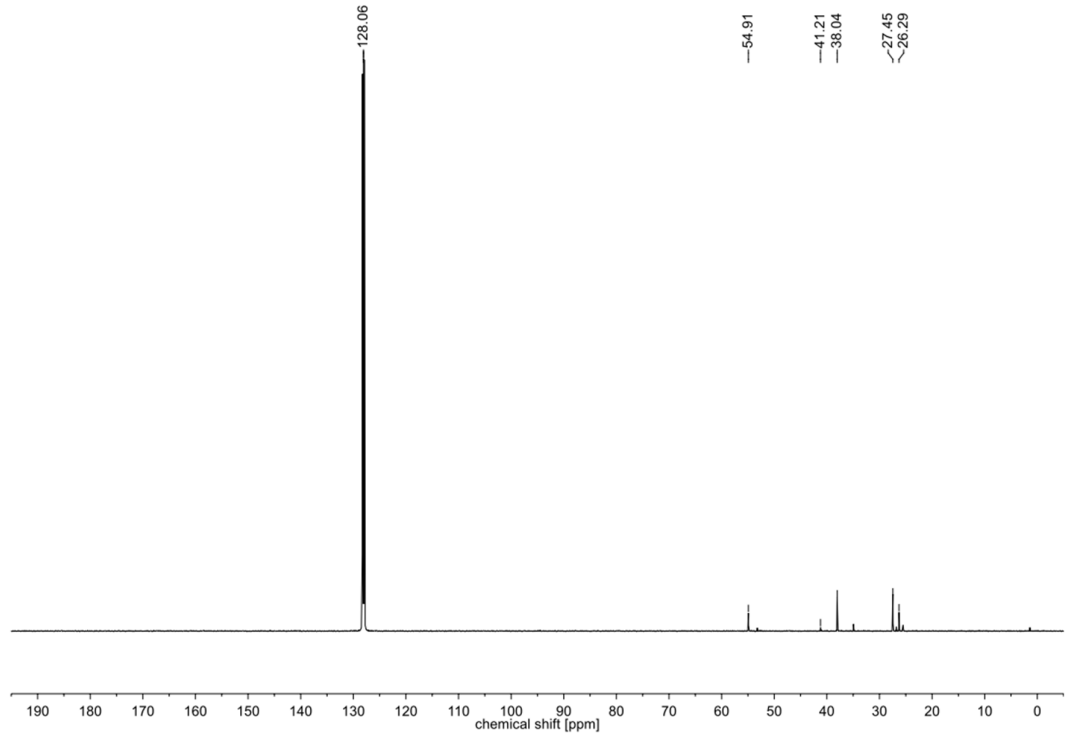

Figure S9 - ^{13}C NMR spectrum of **2-Hf** (125.7 MHz, 305.0 K, C_6D_6).

2.3 ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR Spectra of $[(Cy_2N)_3Ti]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Ti**)

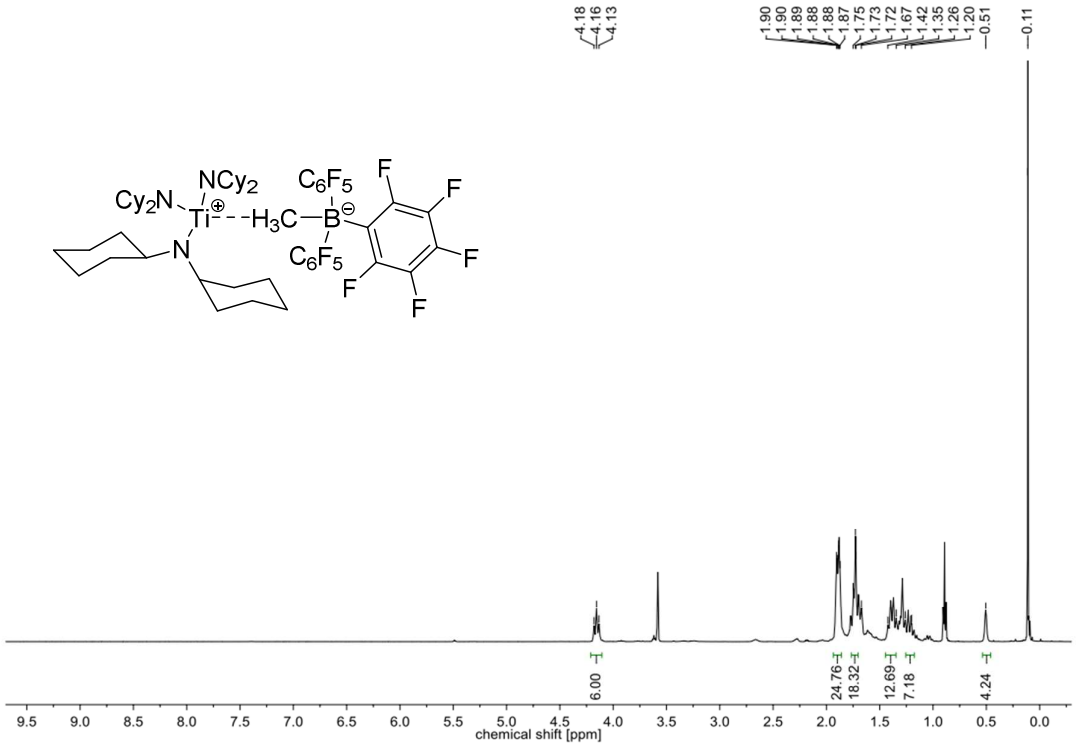

Figure S10 - ^{1}H NMR spectrum of **3-Ti** (499.9 MHz, 305.0 K, THF-d_8).

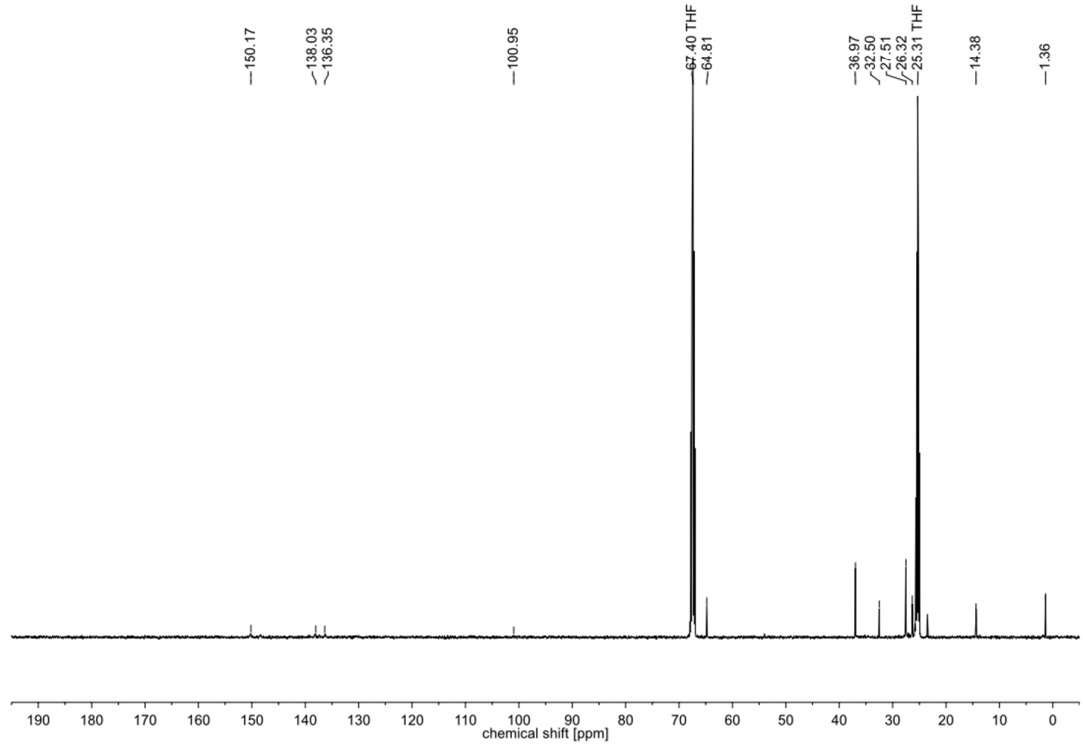

Figure S11 - ^{13}C NMR spectrum of **3-Ti** (125.7 MHz, 305.0 K, THF-d_8).

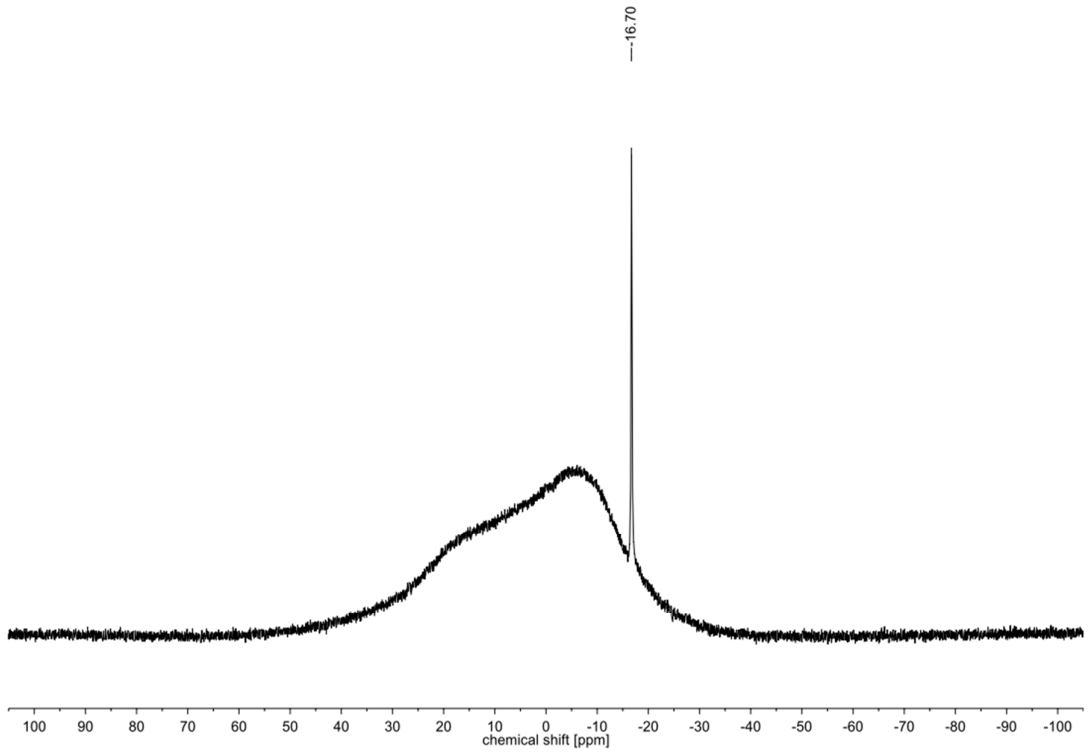

Figure S12 - ^{11}B NMR spectrum of **3-Ti** (160.4 MHz, 305.1 K, THF-d_8).

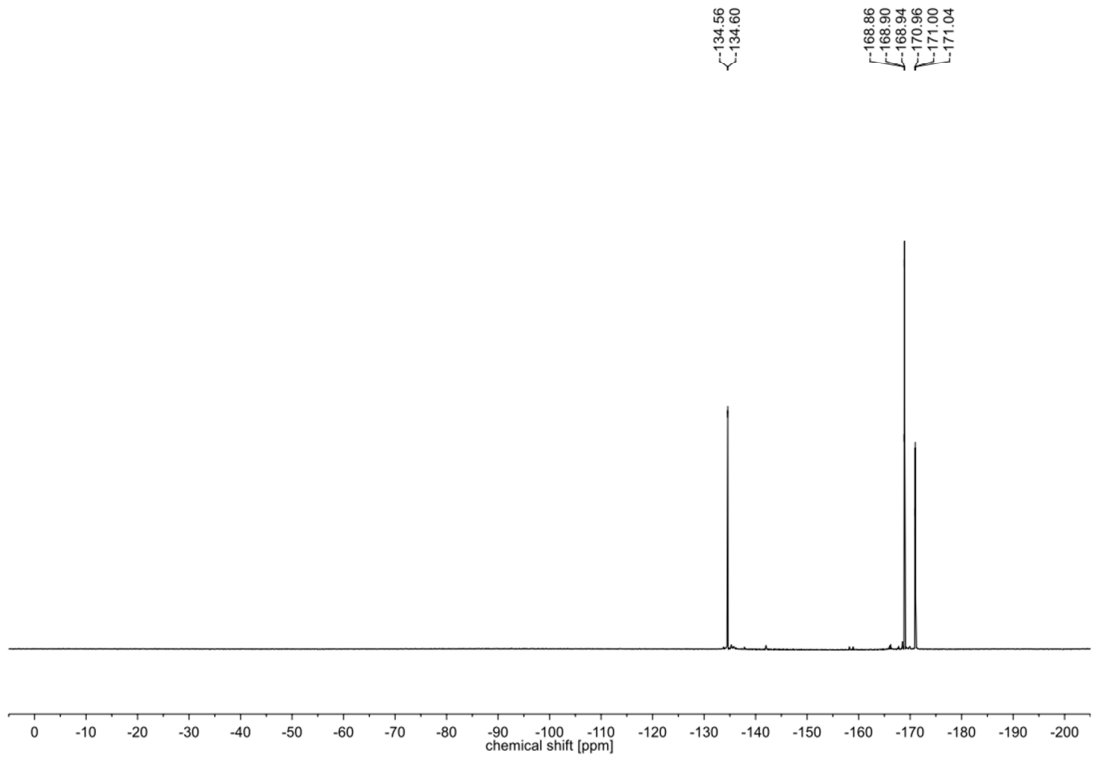

Figure S13 - ^{19}F NMR spectrum of **3-Ti** (470.3 MHz, 305.0 K, THF-d_8).

2.4 ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR Spectra of $[(Cy_2N)_3Zr]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Zr**)

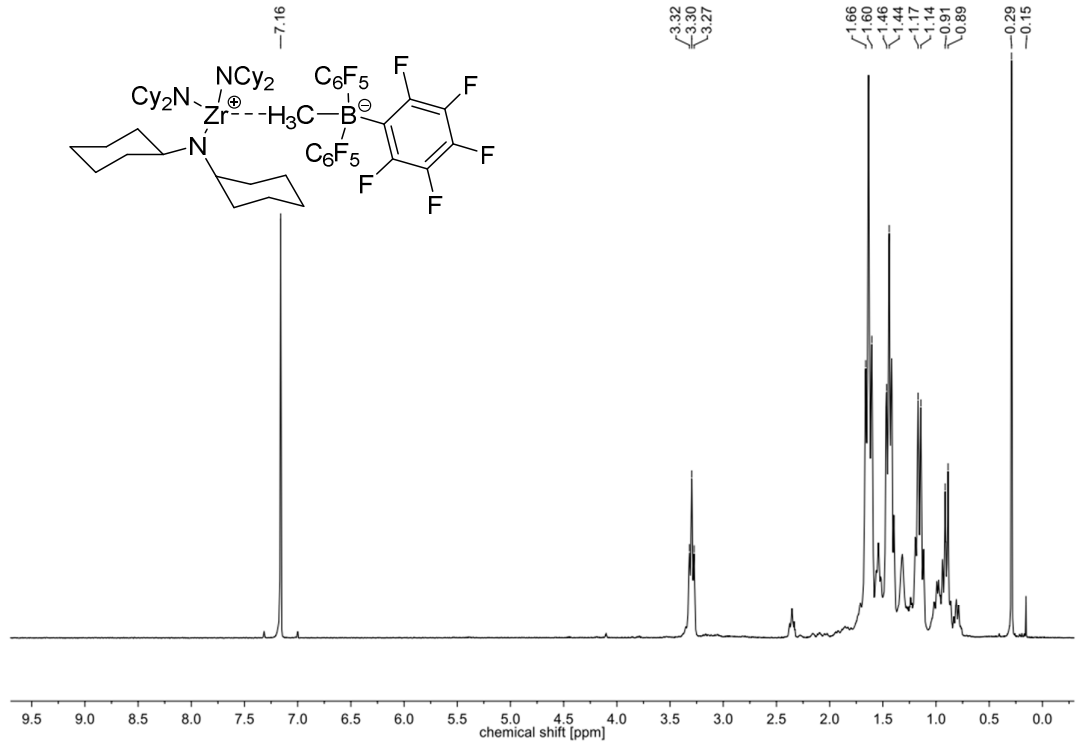

Figure S14 - ^{1}H NMR spectrum of **3-Zr** (499.9 MHz, 305.0 K, C_6D_6).

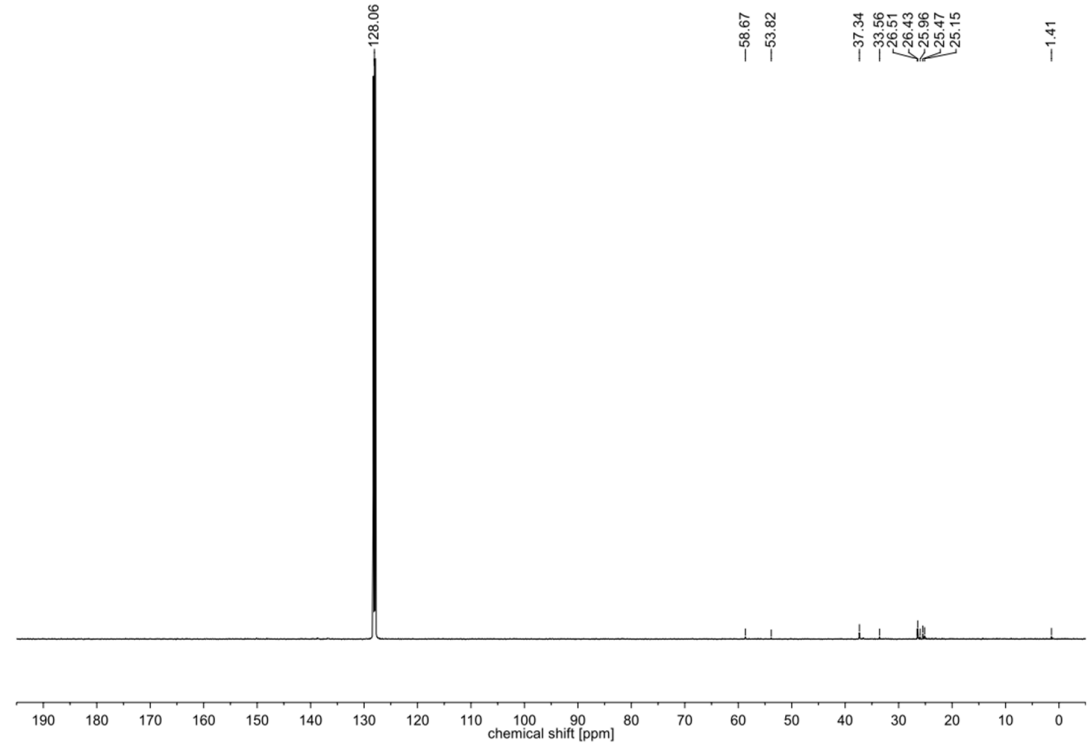

Figure S15 - ^{13}C NMR spectrum of **3-Zr** (125.7 MHz, 305.0 K, C_6D_6).

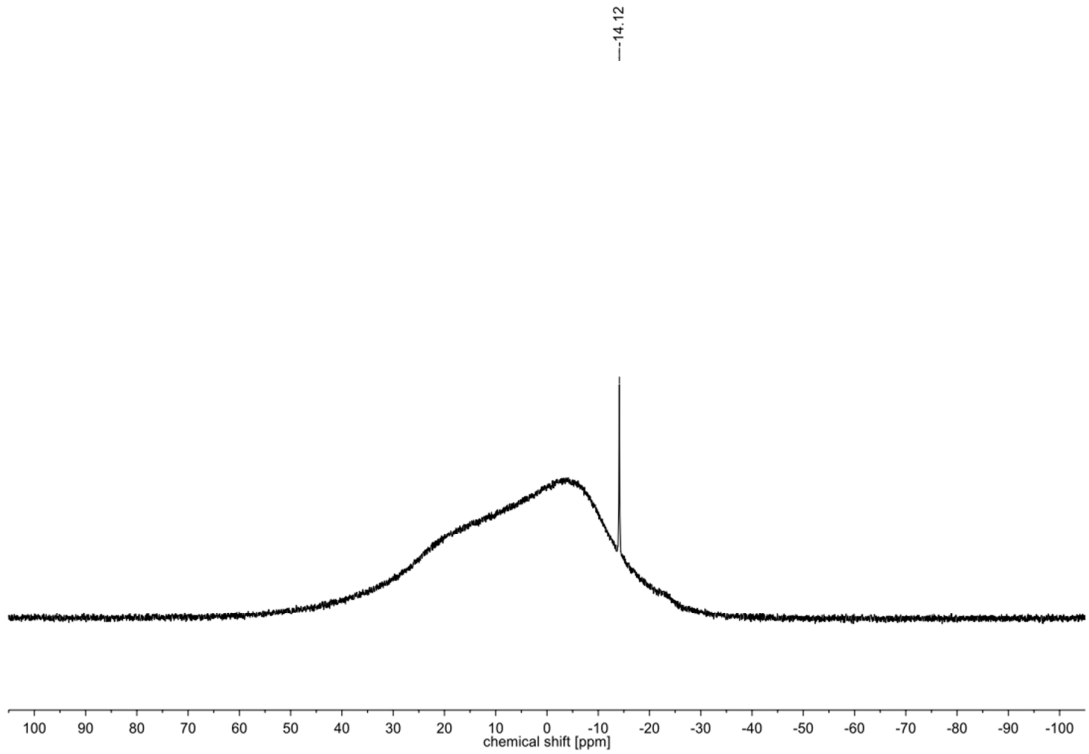

Figure S16 - ^{11}B NMR spectrum of **3-Zr** (160.4 MHz, 305.1 K, C_6D_6).

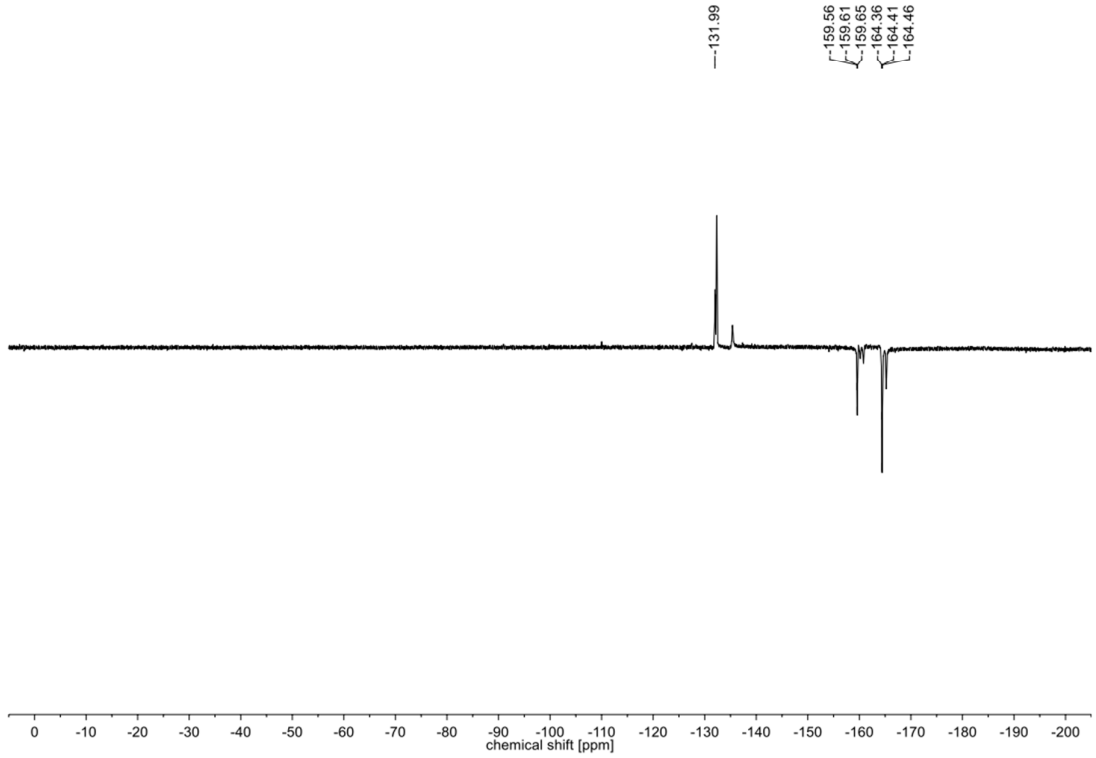

Figure S17 - ^{19}F NMR spectrum of **3-Zr** (470.3 MHz, 305.1 K, C_6D_6).

2.5 ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR Spectra of $[(Cy_2N)_3Hf]^+[(\mu\text{-Me})B(C_6F_5)_3]^-$ (**3-Hf**)

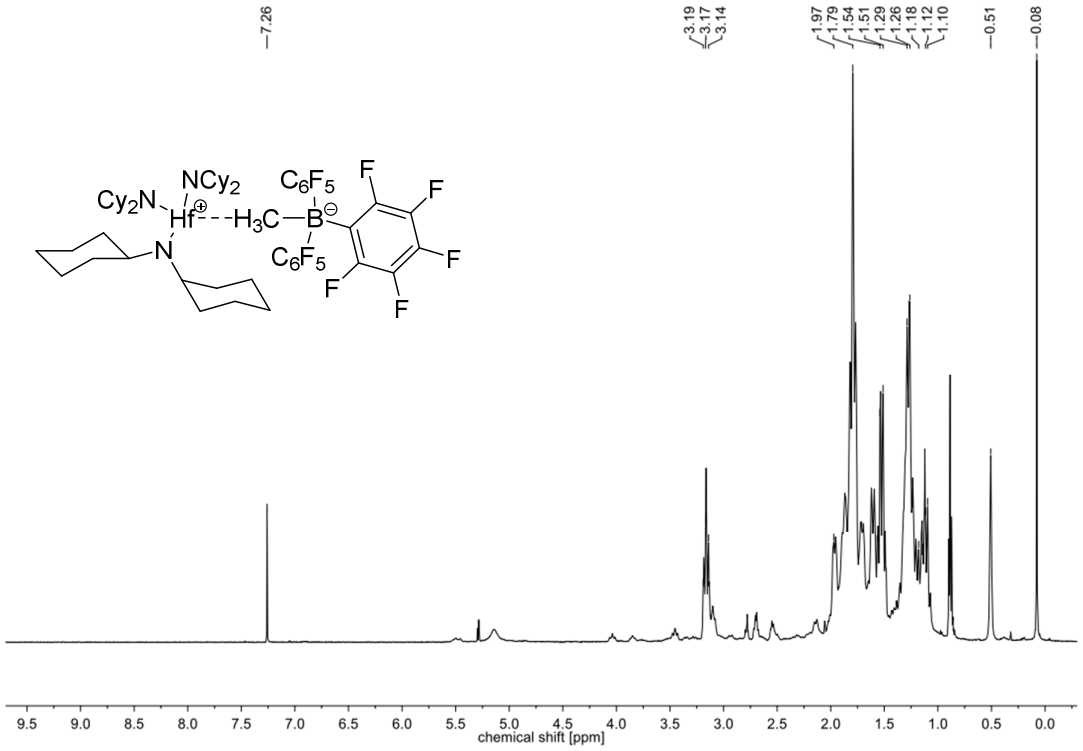

Figure S18 - ^{1}H NMR spectrum of **3-Hf** (499.9 MHz, 305.1 K, $CDCl_3$).

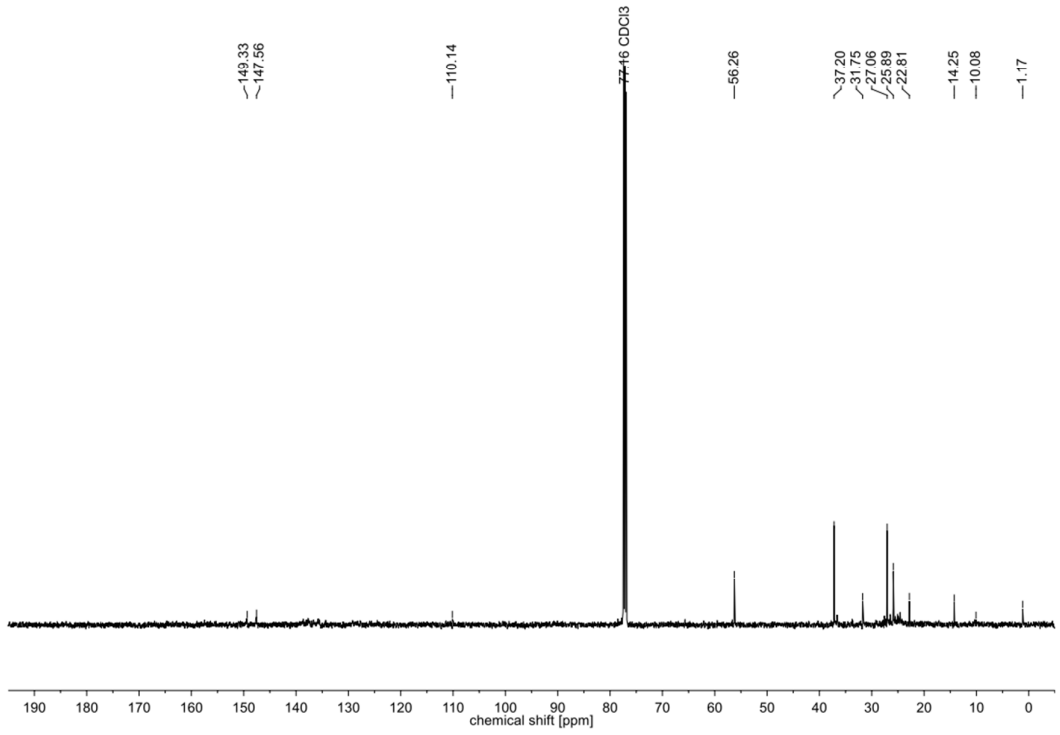

Figure S19 - ^{13}C NMR spectrum of **3-Hf** (125.7 MHz, 305.0 K, $CDCl_3$).

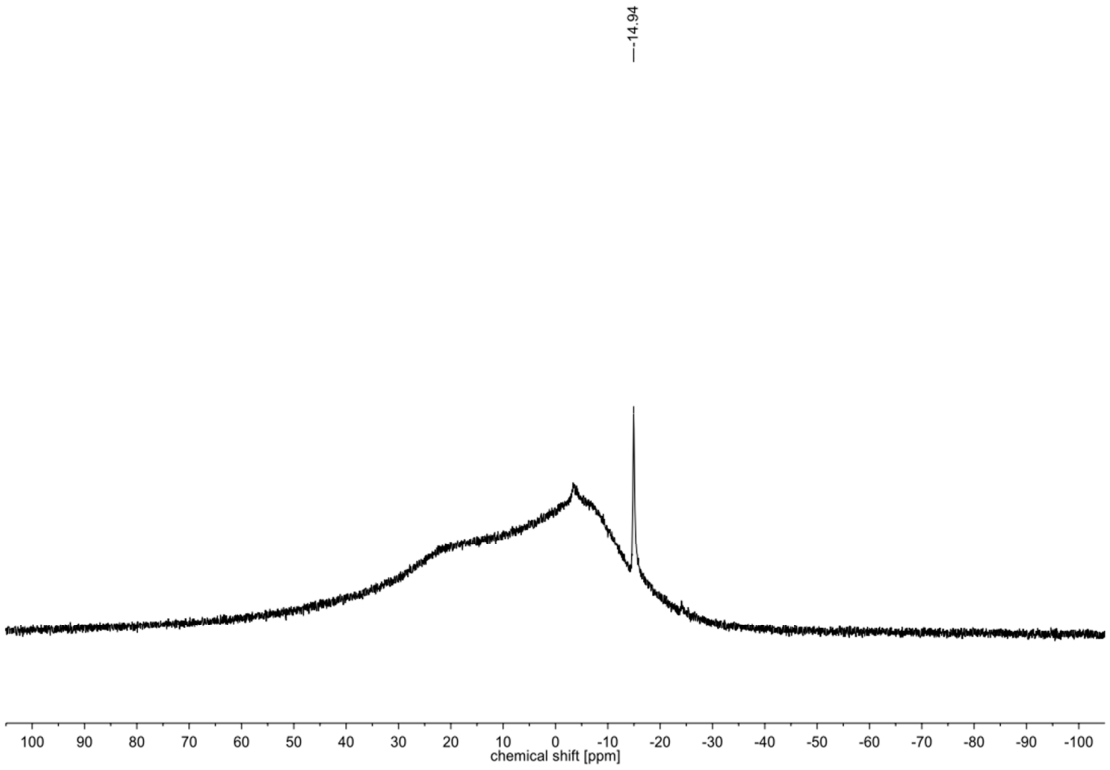

Figure S20 - ^{11}B NMR spectrum of **3-Hf** (160.4 MHz, 305.0 K, $CDCl_3$).

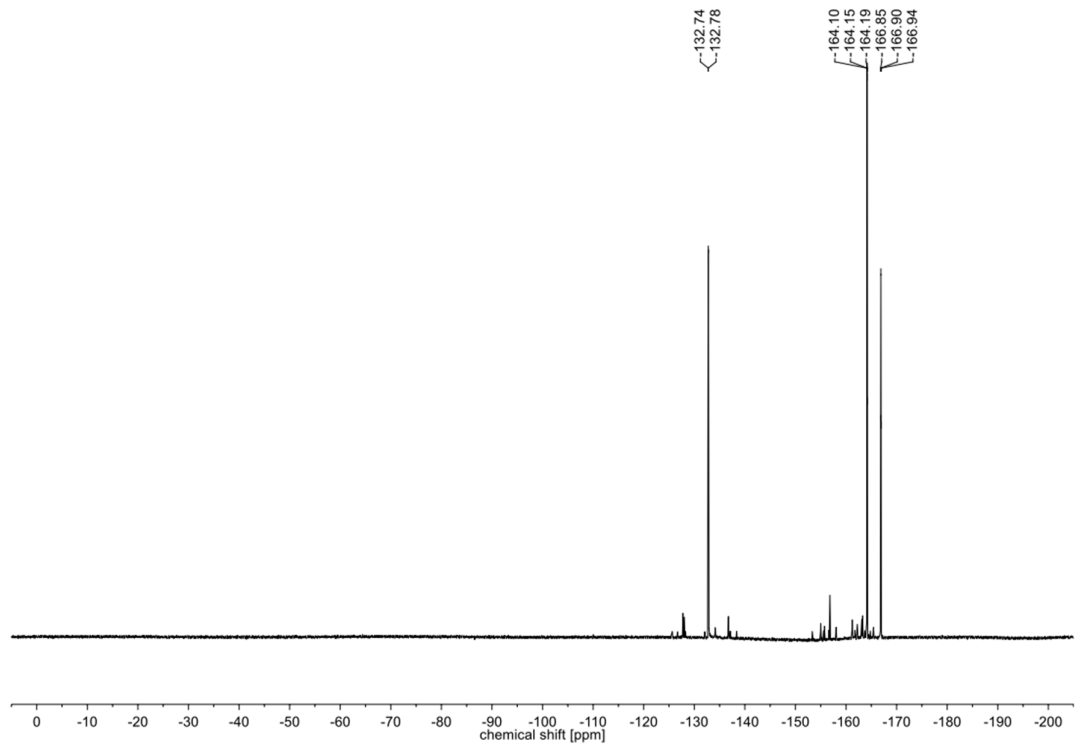

Figure S21 - ^{19}F NMR spectrum of **3-Hf** (470.3 MHz, 305.1 K, $CDCl_3$).